



Soviet-era science, translated into English

PHYSICAL CHEMISTRY

B. V. ERSHLER and V. G. FIRSOV

1961

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196101.98986>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

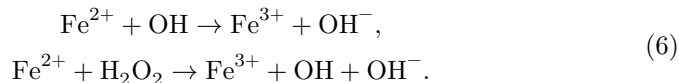
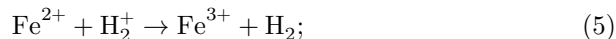
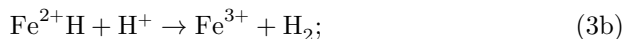
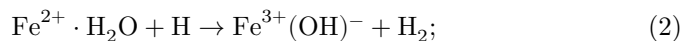
PHYSICAL CHEMISTRY

B. V. ERSHLER and V. G. FIRSOV

THE $I^{1/2}$ LAW IN THE RADIOLYTIC OXIDATION OF IRON IONS BY HYDROGEN ATOMS AND THE MECHANISM OF THE PROCESS

(Presented by Academician A. N. Frumkin, 17 IV 1961)

Haber ⁽¹⁾ was apparently the first to point out the possibility of oxidative reactions of H-atoms, proposing a triple collision of an H-atom, an H⁺ ion, and a molecule of the reducing agent. Weiss ⁽²⁾, as the first stage of the oxidation of Fe²⁺ by H atoms during radiolysis, proposed reaction (1). He regarded the oxidation process as a simple electron transfer according to reaction (5).



This view was supported by Allen and others, but was often called into question. Thus, Jori ⁽³⁾ believed that the H-atom can oxidize in aqueous solution

without the intermediate formation of the ion H_2^+ , for example, by reaction (2). Recently Halpern, Czapski, and others^(4,5) presented arguments in favor of the formation, by reactions (3), of an iron hydride ion as an intermediate product in the radiolytic oxidation by the H-atom. Dainton and Peterson⁽⁶⁾, without excluding the possibility of reaction (1), indicated that the H-atom, which is incapable of oxidizing Fe^{2+} at low pH, may be a solvated electron. The presence of the latter during radiolysis was proposed by Weiss⁽⁷⁾. Thus, there are various opinions regarding the mechanism of oxidation of Fe^{2+} by H atoms during radiolysis. To clarify this mechanism we attempted to use Allen's model and the $I^{1/2}$ laws, which, as we have already indicated^(8,9), make it possible to study radiolysis processes in greater detail.

Thoroughly deaerated solutions with various concentrations of FeSO_4 at different pH values were irradiated in a Co^{60} source at various radiation intensities I (the intensity was determined by irradiation of a solution of ferrous iron in $0.8\text{ N H}_2\text{SO}_4$), and the initial yield of iron oxidation, G , was measured. In addition, the value of G was carefully measured over a broad range of FeSO_4 concentrations in $0.8\text{ N H}_2\text{SO}_4$. As is seen from Figs. 1 and 2, G in $0.8\text{ N H}_2\text{SO}_4$ is almost independent of the FeSO_4 concentration over a range of almost 3 orders of magnitude of concentration and, decreasing with increasing pH, still does not depend on this concentration. When the radiation intensity is changed from some value I_1 to I_2 , the curve of the dependence of G on $\lg[\text{H}^+]$ shifts along the logarithmic axis in quantitative agreement with the theory of the $I^{1/2}$ laws⁽⁸⁾, i.e., the curve does not change its shape and, in its new position, proves to be shifted from its initial position by the amount $\lg(I_2/I_1)^{1/2}$.

As already noted^(8,9), Allen's model includes two approximations: 1) the initial yields of molecules and radicals are considered not to depend on the concentration of acceptors; 2) the equations of homogeneous chemical kinetics are applied to the reactions of the primary products of radiolysis. In our case, the independence of G from the concentration of Fe^{2+} ions at low pH indicates the admissibility of approximation 1) of Allen's model, while the presence of the $I^{1/2}$ law at high pH indicates good quantitative agreement of approximation 2) of this model with experiment for the given radiolytic process.

The substantiation of the quantitative agreement of Allen's model with the radiolysis process on the basis of the $I^{1/2}$ law is quite general^(8,9), since it does not require the introduction of any empirical constants, for example values of the initial yields of H_2 , H_2O_2 , H and OH, or any assumptions about the kinetics and mechanisms of the reactions occurring in solution. Therefore such substantiation appears more convincing than the calculations of the model reported in the literature⁽¹⁰⁻¹³⁾, which require the introduction of numerous empirical constants and at the same time ignore the interaction between radicals born not in one and the same track. It should be noted that the presence of interaction of radicals from different tracks, which in the present case proceeds, possibly, through reaction (4), is clearly seen in Fig. 1. Indeed, the decrease of G with pH indicates that the rate of recombination of oxidizing radicals begins to exceed

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

the rate of their capture by the acceptor, i.e., by the H^+ ion. However, by decreasing I , i.e., by moving the tracks apart from one another, we increase G , i.e., hinder recombination. The hindrance of recombination when the tracks are separated evidently indicates interaction of radicals from different tracks.

Fig. 1. Dependence of the oxidation yield on pH, radiation intensity (in $eV/l \cdot sec$) and concentration of $FeSO_4$ (mN). a –50 mN, b –10 mN, $I_1 = 9.3 \cdot 10^{18}$; v –50 mN, g –10 mN, $I_2 = 3.4 \cdot 10^{17}$; d –5 mN, $I_3 = 2.5 \cdot 10^{16}$; zh –1 mN, $I = 4.8 \cdot 10^{17}$ according to ⁽¹⁶⁾. The solid curves are drawn according to equation (1) at $k_1/k_4^{1/2} = 3 \cdot 10^{-2}$.

Fig. 2. Dependence of the oxidation yield G on the concentration of $FeSO_4$ in 0.8N H_2SO_4 at $I = 9.3 \cdot 10^{18}$ $eV/l \cdot sec$.

The quantitative agreement found here between Allen's model and the radiolysis process makes it possible to refine the mechanism of the latter. The independence of G from the concentration of $FeSO_4$ and its dependence on pH and I indicate that in the slow stage of the radiolytic oxidation of iron the Fe^{2+} ions do not participate, but only H^+ ions do. This excludes the possibility of a significant contribution to the oxidation process from triple-collision reactions, as well as from reactions (2) and (3). Of the reactions proposed in the literature, only reaction (1) is consistent with the data of this experiment, and thus the H^+ ion should here be considered the acceptor of the H atom.

The explicit action of H^+ ions as acceptors of H atoms had already been shown by one of us ⁽¹⁵⁾ in the example of the competition of H^+ and UO_2^{2+} ions for the H atom in the oxidation of Fe^{2+} ions, where no participation of the latter in this competition was likewise observed. Evidently the same phenomenon was observed in ⁽¹⁶⁾, in the example of the competition of H^+ and Fe^{3+} ions for the H atom. The conception of reaction (1) as the slow stage of oxidation by H atoms, and also the conception of competition of H^+ with various acceptors of H, without participation in this competition of the oxidized Fe^{2+} ion, appears to be the only possible explanation of the dependences of G on pH or on the concentration of H acceptors in the absence of such a dependence on the concentration of the oxidized Fe^{2+} ion itself. Taking into account reactions (1) and (4) and writing the equation of the Allen model for the initial yields



we obtain, by the method of stationary states, the equation

$$\left(\frac{100N}{I}\right)^{1/2} \frac{k_1}{k_4^{1/2}} [\text{H}^+] = -\frac{G - n - 2k}{(n + k - \frac{1}{2}G)^{1/2}}, \quad (\text{I})$$

relating G to $[\text{H}^+]$ and I . It agrees well quantitatively with experiment at $k_1/k_4^{1/2} = 3 \cdot 10^{-2}$ (Fig. 1). In deriving equation (I) it was assumed that the particles H_2O_2 , OH oxidize iron according to reactions (6), and H_2^+ according to reaction (5). It is seen from Fig. 1 that the yields m, l, n, k of the primary radiolysis products according to reaction (7) do not depend on pH. Thus, G decreases with increasing pH from 8.2 to ~ 5.0 , which would seem to indicate a decrease in the initial yields of oxidizing particles with increasing pH; however, by decreasing I , even at high pH one can obtain $G = 8.2$, and, consequently, in reality the initial yields m, l, n, k do not depend on pH. This observation is in strict accord with two approximations of Allen's model, which, apparently, is now the basis of the most accurate quantitative theory of radiolysis by γ -radiation in dilute aqueous solutions for a large group of radical acceptors. Indications in the literature⁽¹⁶⁾ concerning the dependence of the yields of H_2 , H_2O_2 , H, and OH on pH were made without taking account of $I^{1/2}$ -regularities in radiolysis. Indeed, Fig. 1 gives the data of⁽¹⁶⁾; they fall on the curve corresponding to the value of I that occurred in⁽¹⁶⁾. The competition of reactions (1) and (4) and the applicability of Allen's model to this process make possible measurement of the activation energy of reaction (1), as was already pointed out by one of us⁽¹⁷⁾. Judging from the magnitude of the constant $k_1/k_4^{1/2}$, this energy must be considerable. Some data on the activation energy of oxidation processes by H atoms have been published by us⁽¹⁸⁾.

Received
6 II 1961

CITED LITERATURE

- ¹ J. D. Ethier, F. Haber, *Naturwiss.*, **18**, 266 (1930).
- ² J. Weiss, *Nature*, **165**, 728 (1950).
- ³ N. Uri, *Chem. Rev.*, **50**, 375 (1952).
- ⁴ G. Czapski, J. Jortner, *Nature*, **188**, 50 (1960).
- ⁵ J. Halpern, G. Czapski et al., *Nature*, **186**, 629 (1960).
- ⁶ F. S. Dainton, D. B. Peterson, *Nature*, **186**, 878 (1960).
- ⁷ J. Weiss, *Nature*, **186**, 751 (1960).
- ⁸ B. V. Ershler, *DAN*, **129**, 866 (1959).
- ⁹ V. G. Firsov, B. V. Ershler, *DAN*, **138**, No. 4 (1961).
- ¹⁰ A. H. Samuel, J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).
- ¹¹ A. K. Ganguly, J. L. Magee, *J. Chem. Phys.*, **25**, 129 (1956).
- ¹² P. J. Dyne, J. M. Kennedy, *Canad. J. Chem.*, **36**, 1518 (1958).
- ¹³ P. J. Dyne, J. M. Kennedy, *Canad. J. Chem.*, **38**, 61 (1960).
- ¹⁴ B. V. Ershler, M. A. Nezhevenko, G. G. Myasishcheva, *DAN*, **126**, 126 (1959).
- ¹⁵ V. G. Firsov, *DAN*, **138**, No. 5 (1961).

- ¹⁶ W. G. Rothschild, A. O. Allen, *Radiation Res.*, **8**, 101 (1958).
¹⁷ B. V. Ershler, Proceedings of the 1st All-Union Conference on Radiation Chemistry, Moscow, 1958, p. 111.
¹⁸ V. G. Firsov, B. V. Ershler, *ZhFKh*, **35**, No. 8 (1961).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.